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# RESONANCE QUASI-PROJECTION OPERATORS: CALCULATION OF AUTOIONIZATION STATES OF $\text{He}^-$

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OPERATORS: CALCULATION OF  
AUTOIONIZATION STATES OF  $\text{He}^-$

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### Abstract

A method is presented to remedy the defects of the projection operator technique for calculating electron resonances in scattering from many electron targets. Specifically it is shown that if the projection operator (i. e. idempotent)  $Q$  is replaced by a quasi-projection operator  $\hat{Q}$  such that  $\lim_{r_i \rightarrow \infty} \hat{Q}\Psi = 0$  as any  $r_i \rightarrow \infty$ , then the spectrum of  $QH\hat{Q}$  is discrete, and can be made to be in essentially a unique correspondence with resonance energies. Relaxation of the idempotency requirement allows us to define two forms of  $Q$  operator. The simpler of the two forms is tested on e-H and e-He<sup>+</sup> systems; the two lowest resonant energies differ by less than 0.01 eV from rigorous  $QH\hat{Q}$  results. For many-electron targets it is further argued that replacement of the exact target eigenfunction ( $\phi_0$ ) by reasonable approximations ( $\tilde{\phi}_0$ ) in constructing  $\hat{Q}$  will affect neither the discreteness of the spectrum  $\hat{Q}H\hat{Q}$  nor the proximity of its eigenvalues to the resonant energies. Calculations of He<sup>-</sup> using two different (open and closed shell)  $\phi_0$ 's and an angle independent total wave function ( $\Psi$ ) are found to differ by 0.01 eV. The open shell ground state has been used with a configuration interaction  $\Psi$  with up to 40 configurations; it gives  $E_{res}(^2S) = 19.386$  eV and a width  $\Gamma =$  . No other resonances are found below the first excited ( $2^3S$ ) target threshold.



## I. INTRODUCTION

The most clean cut technique for calculating resonances in electron collisions with atomic systems arises from the projection-operator formalism of Feshbach.<sup>1</sup> The effectiveness of the method stems from the fact that "Feshbach" resonance energies  $E_n$ , which are part of a continuous spectrum of the Schrödinger equation, are in a unique correspondence with eigenvalues of a projected Schrödinger-like equation whose spectrum is discrete and which can be solved as an ordinary bound state problem. Specifically this means that resonant energies come out automatically and do not have to be hunted for (and perhaps missed) as in a scattering calculation.

The projected problem,  $QHQ \Phi_n = E_n \Phi_n$ , depends on an operator  $Q$  whose complement

$$P = 1 - Q \quad (1.1)$$

is such that it does not change the asymptotic form of the exact (scattering) solution

$$\lim_{r_f \rightarrow \infty} P \Psi = \Psi, \quad (1.2a)$$

so that

$$\lim_{r_f \rightarrow \infty} Q \Psi = 0. \quad (1.2b)$$

To these Feshbach<sup>1</sup> has added the requirement of idempotency:

$$P^2 = P; \quad Q^2 = Q, \quad (1.3)$$

which is equivalent to the statement that  $Q$  and  $P$  are projection operators.

Rigorous calculations using this formalism are restricted to one-body targets, because only in that case can explicit and rigorous P and Q operators be given.<sup>2</sup> In the case of many-electron targets, Feshbach<sup>1</sup> has given a formal expression for these operators which is not really practical, because: (a) it requires knowledge of the exact target wave function  $\phi_0(1,2,\dots,N)$ , (b) it requires the eigen-solutions of a homogeneous integral equation to take care of the antisymmetric identity of scattered and orbital electrons. Problem (a) is common to any scattering problem; in practice it can be handled by using a suitable approximation of  $\phi_0$ . However, problem (b) makes it impractical to use Feshbach's Q for anything but a separable approximation of  $\phi_0$ .

## II. QUASI-PROJECTION OPERATORS

This has led us to reexamine the idempotency requirement. Some consideration shows that the asymptotic conditions (1.2) can be satisfied by  $\hat{P}$  and  $\hat{Q}$  which are not projection operators. Furthermore one can show (cf. Appendix I) that the counterpart of condition (1.2b):

$$\lim_{\text{any } r_i \rightarrow \infty} \hat{Q} \psi = 0 \quad (2.1)$$

leads to a discrete spectrum associated with the Rayleigh-Ritz variational principle

$$\delta \frac{\langle \hat{Q} \psi, H \hat{Q} \psi \rangle}{\langle \hat{Q} \psi, \hat{Q} \psi \rangle} = 0. \quad (2.2)$$

In fact the restriction of a trial set of functions to be quadratically integrable is implicitly equivalent to using a quasi-projection operator on a totality of wave functions which might otherwise include non-vanishing scattering wave functions. In accord with our general theorem, this implicit restriction of quadratically

integrable function leads to the well known and obvious result that diagonalizing the Hamiltonian yields a discrete spectrum of energies. Such a naive procedure yields mostly nonautoionizing states, and methods of picking out the autoionization states from among them have been developed by Holþien, Lipsky and Russek,<sup>4</sup> Taylor et al.,<sup>5</sup> and Perkins.<sup>6</sup> These methods generally go under the name stabilization of roots; unfortunately with the exception of Perkins work<sup>5</sup> (which rigorously applies only to one-electron targets) they do not correspond to an exact prescription nor do they distinguish between Feshbach resonances (i. e., compound atom or core excited) and shape resonances. Furthermore, aside from the work of Hazi et al.,<sup>5,7</sup> one does not get a prescription for the width from this formalism. And finally all these methods implicitly assume the use of a configuration interaction type wave function.

These difficulties derive basically from the fact that  $\hat{Q}$  in these methods is not only implicit but uncontrolled and therefore not necessarily fixed from one calculation to the next. The idea that we shall project puts forward explicit forms for  $\hat{Q}$ . Once a form of  $\hat{Q}$  is given, all the difficulties mentioned above can be readily overcome. Two forms of  $\hat{Q}$  readily present themselves<sup>8</sup>

$$\hat{Q}_a \equiv \prod_{i=1}^{N+1} (1 - P_i) \quad (2.3)$$

and

$$\hat{Q}_b \equiv 1 - \sum_{i=1}^{N+1} P_i \quad (2.4)$$

In both cases we define

$$\hat{P}_{a,b} \equiv 1 - \hat{Q}_{a,b} \quad (2.5)$$

and the projectors  $P_i$  are given by

$$P_i = \sum_{M_L, M_S} \phi_0(\chi_1, \dots, \chi_{i-1}, \chi_{i+1}, \dots, \chi_{N+1}) \langle \phi_0(\chi_1, \dots, \chi_{i-1}, \chi_{i+1}, \dots, \chi_{N+1}) | \quad (2.6)$$

Note that the subscript labelling  $P_i$  refers to the particle coordinates which are absent from the  $\phi_0$ . Thus  $i$  labels the scattered particles. The  $x$  refers to both spatial and spin (one-half) coordinates of each particle. The explicit inclusion of spin in these operators makes them in principle applicable to many body targets where Feshbach's form,<sup>1</sup> in addition to the difficulties mentioned above, appears to depend only on spatial coordinates. Notwithstanding this,  $\hat{Q}_a$  is more complicated to use, particularly if one contemplates increasing the accuracy of  $\phi_0$  as well as  $\Psi$ .

In using  $\hat{Q}_b$  we shall see directly below that in the discrete set of states associated with  $\hat{Q}_b \hat{Q}_b$  there may be states which do not correspond to auto-ionization states. However there are only a finite number of such spurious states and they can be identified in advance.

### III. ONE-ELECTRON TARGETS

To see this consider the one electron target case in which the total wave function can be written

$$\Psi(\chi_1, \chi_2) = \Phi(\underline{r}_1, \underline{r}_2) \chi_S(1, 2) \quad (3.1)$$

where  $\chi_S$  is the total singlet ( $S = 0$ ) or triplet ( $S = 1$ ) spin function. In calculating the variational principle (2.2), one will be led to calculate matrix elements of  $\hat{Q}_b$  (called  $Q$  hereinafter) between two different functions,  $\langle \Psi_1 \hat{Q}_b \Psi_2 \rangle$  where  $\Psi_1$  and  $\Psi_2$  are of the form of (3.1).  $[\Psi_2]$  can be considered to be  $HQ\Psi$  of Eq. (2.2) for

example]. Let us expand the spatial functions  $\Phi_i$  associated with  $\Psi_i$  in terms of a complete set of product target eigenstates  $\theta_n(\mathbf{r})$ :

$$\Phi_i = \sum_n C_{nn}^{(i)} \vartheta_n(r_1) \vartheta_n(r_2) \delta_{S0} + \sum_{n>v} \sum_{n'v} C_{n'v}^{(i)} \left[ \vartheta_n(r_1) \vartheta_{v'}(r_2) \pm \vartheta_n(r_2) \vartheta_{v'}(r_1) \right] \quad (3.2)$$

where  $\delta_{S0}$  explicitly indicates that the diagonal terms only arise in singlet states.

Straightforward substitution of (6) and (8) into  $\langle \Psi_1 \hat{Q} \Psi_2 \rangle$  leads to

$$\langle \Psi_1 \hat{Q} \Psi_2 \rangle = \langle \Phi_1, \Phi_2 \rangle_{S0} - \langle \langle \Phi \vartheta_0 \rangle_1, \langle \vartheta_0 \Phi \rangle_2 \rangle, \quad (3.3)$$

where from (2.4)  $\hat{Q}$  is here explicitly

$$\hat{Q} = 1 - P_1 - P_2. \quad (2.5a)$$

In (3.3) the subscripts on the kets indicates the integrated coordinate in the integral symbolized by the bra-ket. Now substituting (3.2) into (3.3) we obtain after some manipulation,

$$\langle \Psi_1 \hat{Q} \Psi_2 \rangle = - C_{00}^{(1)} C_{00}^{(2)} \delta_{S0} + \sum_{n>v} \sum_{n'v'} C_{n'v'}^{(1)} C_{n'v'}^{(2)}. \quad (3.4)$$

This says that arbitrary matrix elements of  $\hat{Q}$  contain only one term referring to the ground state in the singlet case ( $S = 0$ ) and no terms in the triplet case ( $S = 1$ ). Thus in the singlet eigenvector spectrum there will be one eigenvector with that coefficient large; for all other eigenvectors that coefficient will be small. All other coefficients referring to the ground state in the expansion

do not even arise in the calculation (i. e., are zero). The corresponding eigenvalue spectrum will therefore reflect that fact by having one low eigenvalue corresponding to ordinary elastic scattering (or a true bound state of the compound system, as the case may be). All remaining eigenvalues refer to doubly excited (i. e. autoionization) states. In the triplet case there are no spurious states, and in fact the operator  $\hat{Q}$  then becomes identical to the idempotent  $Q$  of Hahn *et al.*<sup>2</sup>

The general statement is that the number of terms in  $\langle \Psi_1 \hat{Q} \Psi_2 \rangle$  with indices referring to the ground state of the target is the number of spurious autoionization states in  $QHQ$ , and they are the lowest ones that arise. We shall reexamine what this number is in the e-He system below. In Table I we give results for  $^1S$  autoionization states of the e-He<sup>+</sup> and e-H systems using a Hylleraas form for  $\Phi$ :

$$\Phi(r_1, r_2) = e^{-\gamma(r_1+r_2)} \sum_{l,m,n}^N C_{l,m,n} (r_1^l r_2^m + r_1^m r_2^l) r_{12}^n. \quad (3.5)$$

The second and third eigenvalues then correspond to the first two resonant energies. Note both the convergence as function of the number of terms  $N$  and the proximity of the essentially converged 50 term values to precision, rigorous  $Q$ -operator results.<sup>9</sup> ( $E_0$  is the ground state energy of He<sup>+</sup> and H respectively.)

#### IV. TWO-ELECTRON TARGETS

We now turn to the electron-helium system which is of chief interest here, because it is the simplest example of a more than one-electron target. We consider in particular the doublet states which are the only ones that can nonrelativistically autoionize below the first excited state ( $2^3S$ ) of helium. The doublet functions can be written

$$\Psi = \sum_{\text{cyclic } ijk} \Phi(r_i, r_j; r_k) \chi_0(ij) \chi_{1/2}(k) \quad (4.1)$$

where  $\chi_0$  and  $\chi_{1/2}$  are the spin zero function (of particles  $i$  and  $j$ ) and spin  $1/2$  function of particle  $k$  respectively. The sum goes over cyclic permutations, and the spatial function is again labelled by  $\Phi$ , but here it is a function of three vectors,  $r_i, r_j, r_k$ . It can be constructed to be an eigenfunction of whatever angular momentum  $L$  one chooses to make it, so that the quantum states it describes are appropriately labelled  $^2L$ . Finally in order to be completely antisymmetric,  $\Phi$  must be symmetric in its first two arguments:

$$\Phi(r_i, r_j; r_k) = + \Phi(r_j, r_i; r_k). \quad (4.2)$$

We now want to determine  $\langle \Psi_1 \hat{Q} \Psi_2 \rangle$  where in the present case:

$$\hat{Q} = 1 - P_1 - P_2 - P_3. \quad (2.5b)$$

Again straightforward reduction including spin inner products leads to

$$\begin{aligned} \frac{1}{3} \langle \Psi_1 \hat{Q} \Psi_2 \rangle &= \langle \Phi_1(12;3) \Phi_2(12;3) \rangle - \langle \Phi_1(12;3) \Phi_2(23;1) \rangle \\ &\quad - \{ \langle \langle \Phi_1(12;3) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(12;3) \rangle \rangle \\ &\quad - \langle \langle \Phi_1(23;1) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(12;3) \rangle \rangle \\ &\quad - \langle \langle \Phi_1(12;3) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(23;1) \rangle \rangle \\ &\quad + \langle \langle \Phi_1(23;1) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(23;1) \rangle \rangle \} \quad (4.3) \end{aligned}$$

To analyze this further we expand  $\Phi$  in terms of a complete set of helium eigenstates  $\phi_n$  and associated one-particle functions  $\theta_m$ :

$$\Phi_i(12;3) = \sum_{n,m} C_{nm}^{(i)} \varphi_n(r_1, r_2) \vartheta_m(r_3) \quad (4.4a)$$

which in an obvious notation we rewrite

$$\Phi_i(12;3) = \sum_{n,m} C_{nm}^{(i)} \Phi_{nm}(12;3). \quad (4.4b)$$

We now make a basic assertion which is motivated by the fact that  $\phi_0$  is largely  $(1s)^2$  in character, so that by the exclusion principle no  $\theta_m$  in (4.4a) will contribute to any process if it too is  $(1s)$  (i.e. nodeless) in character. Under these circumstances the  $\theta_m$  being used in (4.4) can always be selected such that (for all  $m$ )

$$\int \vartheta_m(r_i) \varphi_0(r_1, r_2) dr_i = 0, \quad i=1, 2. \quad (4.5)$$

According to our basic criterion we must examine (4.3) for terms connecting to the ground state: i.e. when  $\Phi_1, \Phi_2$  are replaced by  $C_{0m}^{(1)}\Phi_{0m}$  and  $C_{0\mu}^{(2)}\Phi_{0\mu}$  respectively. Again straightforward substitution yields:

$$\langle \Phi_1(12;3) \Phi_2(12;3) \rangle = C_{0m}^{(1)} C_{0\mu}^{(2)} \delta_{m\mu} \quad (4.6)$$

$$\langle \langle \Phi_1(12;3) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(12;3) \rangle \rangle \rightarrow C_{0m}^{(1)} C_{0\mu}^{(2)} \delta_{m\mu} \quad (4.7)$$

All other terms in (4.4) give zero when (4.5) is used. Thus

$$\frac{1}{3} \langle \Psi_1 \hat{Q} \Psi_2 \rangle_{0m, 0\mu} = \left( C_{0m}^{(1)} C_{0\mu}^{(2)} - C_{0m}^{(2)} C_{0\mu}^{(1)} \right) \delta_{m\mu} = 0. \quad (4.8)$$

In other words  $\hat{Q} (= \hat{Q}_b)$  contains no spurious states in the helium case!



In Appendix II we have shown that if a closed shell target function is represented by a single Slater determinant, then  $\hat{Q}_a = \hat{Q}_b$ , and for both  $\hat{Q}^2 = \hat{Q}$  which implies  $P^2 = P$ .<sup>10</sup> Thus there are never any spurious eigenvalues for closed shell targets. Although we have not shown it except in the case of helium, we believe that this absence of spurious eigenvalues holds even if one represents the closed shell by a more elaborate wave function than a single Slater determinant. Finally we believe that if one uses the quasi-projection operator  $\hat{Q}_a$ , it will eliminate all spurious autoionization states below the first excited state of any target atom or ion.

What about the necessity of using an approximate ground state  $\tilde{\phi}_0$ ? We first point out that if one replaces the eigenfunctions  $\phi_n$  of Eq. (15) by approximate orthonormal eigenfunctions  $\tilde{\phi}_n$ , that all the steps go through as before and quasi-projection operators constructed from  $\tilde{\phi}_0$  will therefore eliminate all but a finite number of states containing  $\tilde{\phi}_0$ . The question arises, however, whether the true ground state  $\phi_0$  which may be present in the approximate excited states, may not effectively reenter the spectrum or even worse convert it from a discrete to a continuous one.

Our answer to these questions is first to point out that the mere presence of some ground state in a function does not imply anything about the energy associated with that function. Consider for example the N-electron target system. If we take a linear combination of the approximate ground and first excited state

$$\tilde{\psi} = C_0 \tilde{\phi}_0 + C_1 \tilde{\phi}_1,$$

then the Hylleraas-Undheim theorem<sup>11</sup> says that the diagonalization of the N-electron Hamiltonian will yield eigenvalues  $\tilde{E}_0$  and  $\tilde{E}_1$  which are greater than true energies  $E_0$  and  $E_1$ , respectively. Nevertheless if one expands the corresponding eigenfunction  $\tilde{\psi}_1$  of the first excited state, it will in general contain a non-zero amount of the true ground state  $\phi_0$ . What the Hylleraas-Undheim theorem in effect guarantees is that the amount of  $\phi_0$  in  $\tilde{\psi}_1$  is sufficiently small so as not to ruin the bound.

The above example is not rigorously applicable to the case at hand, because it requires the diagonalization for both eigenvalues be done simultaneously<sup>12</sup> and it is confined to the N-electron problem, whereas here we go from the N to the N + 1 electron system.

This question has been further studied by Hahn.<sup>12</sup> By explicit calculation he has shown in the <sup>1</sup>S e-H system that simple orthogonalization to an approximate ground state can produce an excited target state energy below the true excited state energy. In those cases the H<sup>-</sup> autoionization state energies can also appear below the true excited state energy, even though with his crude total wave function there should be no such autoionization states. However even in those cases the ordering is never reversed, i.e. the autoionization state energies always appear above the lowest excited state energy associated with a function orthogonal to the approximate ground state.

It is clear therefore that the intelligent thing to do in judging the reality of an autoionization state is to compare its energy with the lowest energy one can achieve with an ansatz orthogonal to the approximate ground state being used. Hahn<sup>12</sup> has further argued that simple orthogonalization will prevent the excited state from descending too far below the true excited state.

Before turning to the calculations we make one final point to make more credible the fact that (2.2) can give rise to a discrete spectrum even when  $\tilde{\phi}_0$  used in  $Q$  is not exact. The calculational problem defined by (2.2) is a completely different one from the variational principle for  $H$  itself. Even if one used an exact solution of  $H\Psi = E\Psi$  there is no reason to expect that it would have any special minimal or stationary properties with respect to (2.2). To be sure there will be extra energy shifts associated with the use of  $\hat{Q}$  (in place of  $Q$ ) and with the use of  $\tilde{\phi}_0$  (in place of  $\phi_0$ ), however one has every right to believe these shifts will be small providing the approximations are reasonable. A minimum condition for a reasonable  $\tilde{\phi}_0$  is that its energy  $\tilde{E}_0$  is such that

$$E_0 \leq \tilde{E}_0 < E_1 \quad (4.9)$$

## V. CALCULATED RESULTS, e-He SYSTEM

We have done two independent sets of calculations for the autoionization states of  $\text{He}^-$  below the first excited state ( $2^3S$ ) of He. The first is strictly for  $^2S$  states using a spatial function

$$\Phi(r_1, r_2; r_3) = e^{-[\alpha(r_1+r_2)+\gamma r_3]} \sum_{l,m,n} C_{lmn} (r_1^l r_2^m + r_1^m r_2^l) r_3^n, \quad (5.1)$$

and two forms of the He ( $^1S$ ) ground state, a closed shell

$$\tilde{\phi}_0^{(\text{closed})} = e^{-\frac{27}{16}(r_1+r_2)} \chi_0(12) \quad (5.2)$$

and an open shell<sup>13</sup>

$$\tilde{\phi}_0^{(\text{open})} = [e^{-(2.1832r_1 + 1.1886r_2)} + (1 \leftrightarrow 2)] \quad (5.3)$$

The purpose of this first set of calculations was to confirm that the lowest eigenvalue was convergent to a value well in the continuum of the e-He spectrum and to ascertain that the results were reasonably insensitive of the form of the ground state. For it is to be emphasized that in spite of its simplicity the open shell  $\tilde{\phi}_0$  of Eq. (5.3) is truly non-separable, and cannot even be expressed as a single Slater determinant. Furthermore the ground state energies coming from these two functions are quite different from each other:

$$\tilde{E}_0^{(closed)} = -77.476 \text{ eV}, \quad \tilde{E}_0^{(open)} = -78.234 \text{ eV}.$$

Nevertheless the actual results, given in Table II, relative to the "exact" ground state energy  $E_0 = -79.0016 \text{ eV}$ <sup>14</sup> reveal amazing insensitivity to these differences. The results are also significant, because, to our knowledge, they are the first completely free variational calculations [it is emphasized that no restrictions whatsoever are put on the parameters in (5.1)] for a more than one electron target which converge to a non zero value in the continuous spectrum! (This statement is intended to apply only to Rayleigh-Ritz type methods applied to non-complex energy calculations.)

We have also calculated the width of this resonance using the general formula<sup>15</sup>

$$\Gamma = 2k | \langle \hat{P} \Psi' | H | \hat{Q} \Psi \rangle |^2 \quad (5.4)$$

In this formula  $\hat{Q}\Psi$  is the resonant function associated with (5.1) and (2.5b). The non-resonant scattering function  $\Psi'$  is taken to be of the exchange approximate form; i.e.  $\Phi$  in (4.1) is replaced by  $\Phi'$

$$\Phi(r_1, r_2; r_3) = \tilde{\varphi}_0(r_1, r_2) [u(r_3)/r_3] \quad (5.5)$$

The scattered orbital  $u(r_3)$  is determined from the exchange approximation integro-differential equation<sup>16</sup> and the normalization assumed in (5.4) is<sup>15</sup> (Rydberg units are used throughout.)

$$\lim_{r \rightarrow \infty} u(r) = \frac{1}{k} \sin(kr + \eta) \quad (5.6)$$

$k^2$  is the scattering energy at resonance:

$$k^2 = \hat{E}_i - \tilde{E}_0 \quad (5.7)$$

Finally the form of  $\tilde{\varphi}_0$  used in deriving the scattering equation is the same one for which each resonance calculation is done.

The width is expected to be more sensitive to the approximate form of  $\tilde{\varphi}_0$  since (5.4) is not a stationary expression. The last columns are expected to bear this out, yet they are expected to be close enough to each other as well as to the experimental value (cf. Table III) to give confidence that we are indeed describing the famous 19.3 eV ( $^2S$ ) resonance first discovered by Schulz.<sup>17</sup>

It is to be emphasized in this connection that the energy of these initial calculations would not allow us to predict such a resonance, because it is above the first excited ( $2^3S$ ) state<sup>14</sup> of He ( $E_1 = 19.8202$  eV). (Note that since the first excited ( $2^3S$ ) state of He has opposite symmetry from the ground state ( $1^1S$ ) that any portion of the excited state in (5.1) must correspond to an energy equal to or greater than the true excited state. Concerning the first excited singlet ( $2^1S$ ) state, cf. the last paragraph of the paper, p. 19.) Since our purpose has been to construct a variationally sound, interpretatively unambiguous, and hence predictive method

of computing resonances, we have therefore undertaken a second set of calculations based on a much more general wave function than (5.1), which we now describe.

The wave function is a general configuration interaction wave function which can be written

$$\psi_{L, S=1/2} = \sum_{\{m\}} a \left\{ C_{\{m\}} R_{n_1}(r_1) R_{n_2}(r_2) R_{n_3}(r_3) X \right. \\ \left. y(l_1 l_2 L; l_3; L) s(\frac{1}{2} \frac{1}{2} S_1; \frac{1}{2}; \frac{1}{2}) \right\} \quad (5.8)$$

Here  $a$  is the antisymmetrizer;  $y$  are the orbital angular eigenfunctions describing particles 1 and 2 coupled to give  $L_1$  which in turn is coupled to the  $l_3$  of the third electron to give the total orbital angular of the state  $L$ . Similarly with the spins – except here there are only two possible values of the intermediate spin  $S_1 = 0, 1$ . For  $S_1 = 0$  (5.8) is of the general form of (4.1) and the spatial function must be symmetric in its first two arguments (4.2). If  $S_1 = 1$ , however, the spatial function is antisymmetric in its first two arguments. The radial orbitals have the Slater form

$$R_n(r) = e^{-\alpha r} r^{n-1} \quad (5.9)$$

In general there are as many linear parameters as there are sets  $\{n\}$  where

$$\{n\} \equiv \{n_1, n_2, n_3; (l_1, l_2) L_1, l_3; S_1, L\} \quad (5.10)$$

For each (unantisymmetrized) term there are in principle three non-linear parameters, however this choice is somewhat restricted by the requirement that

the term not vanish when antisymmetrized (for example we know trivially that all the  $n_i, l_i$  and  $a$  of the orbital in (5.8) cannot be the same). In practice the number of nonlinear parameters used is very much smaller than the maximum, but nevertheless of sufficient number to give accurate results.

The program for diagonalizing  $\hat{Q}H\hat{Q}$  automatically searches in the non-linear parameter space chosen for the minimum of a specified root. It is of interest to note that the modification of the original program (to minimize  $H$ ) consisted of adding about one hundred IBM cards to the original program. This is indeed a significant fact for other workers with an energy minimization program available, if they want to calculate autoionization states.

All calculations in this set were done using the open shell ground state (5.3). An example of results of an intermediate calculation based on a twelve configuration expansion is given in Table III. This Table shows that the expansion contained seven nonlinear parameters (1s, 2s, 3s, 2p, 3p, 4s, 4p) of which three (3s, 4s, 4p) were varied in this calculation. The program automatically varies the particular nonlinear parameters in order to minimize a specific eigenvalue in this case the first. One can see that the eigenvalue has been lowered decisively below the  $2^3S$  threshold and is already within 0.1 eV of the experimental value<sup>18</sup>

$$E_{exp}(^2S) - E_0 = 19.33 \pm .03 \text{ eV} \quad (5.11)$$

We are presently completing a 40 configuration calculation with the result

$$E_1(^2S) - E_0 = 19.386 \text{ eV} \quad (5.12)$$



which should be within 0.01 eV of the converged value based on the variational principle (2.2) and the open shell ground state (5.3). The difference between our value and experiment is gratifying. Nevertheless it indicates that the major part of the shift comes from the inexact ground state.

The intrinsic shift is expected to be of the same order of magnitude as (but generally smaller than) the width. The latter has been estimated by Cooper<sup>19</sup> from an analysis of various experiments to be  $\Gamma = 0.004$  eV, which is surprisingly the same as our angle-independent calculation (Table II). Gibson and Dolder<sup>20</sup> have measured a width  $\Gamma = 0.008$  eV. The width calculation based on our configuration interaction wave function has not as yet been completed, but it would be very surprising if it turns out to be the same as that in Table II. We believe that the larger experimental value is the more likely one.

Other resonances below the first excited ( $2^3S$ ) threshold have been reported.<sup>19,20,21</sup> In an effort to confirm these, we have minimized the second eigenvalue of  $\hat{Q}H\hat{Q}$  with our 40 term configuration interaction wave function. We find a lowest second eigenvalue to be  $\mathcal{E}_2 = 19.843$  eV, which is 0.023 eV above the  $2^3S$  state and thus it does not correspond to a resonance. We also intend to calculate  $^2P$  states, however it is extremely unlikely that any will occur below the first threshold. This is because the  $^4P$  state (which is truly a bound state in the nonrelativistic limit) is barely bound<sup>22</sup> [ $E(^4P) = 19.741$  eV] and since  $^2P$  states generally lie higher than  $^4P$  states by more than the difference between  $E(^4P)$  and  $E(2^3S)$ . Thus the prognosis for the existence of other resonances beyond the single  $^2S$  resonance below the first excited state is bleak.



In order to complete the argument that our lowest  $\epsilon_1$  ( $^2S$ ) eigenvalue does indeed correspond to a resonance, we must show that the lowest  $2^1S$  threshold obtainable from a function orthogonal to the approximate  $\tilde{\phi}_0$  is above  $\epsilon_1$  ( $^2S$ ). [If this weren't so, the state might correspond to elastic scattering from such an approximate  $2^1S$  state.] We have done a reasonably definitive calculation of this energy. In fact such a calculation can be done in terms of an idempotent projection operator  $q(12)$ , where

$$q(12) \equiv 1 - \tilde{\phi}_0 \langle \tilde{\phi}_0$$

by minimizing

$$\frac{\int \langle q \psi(12) | H | q \psi(12) \rangle}{\langle \psi(12) | q | \psi(12) \rangle} = 0.$$

Note that this is strictly an  $N = 2$  particle problem [as opposed to (2.2)]. Using the Hylleraas form, (3.5) for  $\Psi$  we obtain a minimum for  $n = 50$  terms at  $\gamma \cong 1.2$  corresponding to

$$E_{2^1S} - E_0 = 20.601 \text{ eV}.$$

This is indeed above the  $2^3S$  threshold, which completes our demonstration, (but it is slightly below the exact  $2^1S$  threshold).

Appendix I  
Discreteness of Spectrum of  $QHQ$

Let us rewrite equation (4)

$$\mathcal{H}\gamma = \varepsilon\gamma \quad (\text{A1.1})$$

In this form the considerations of this appendix will be seen to apply to the Schrödinger equation itself ( $\mathcal{H} = H$ ) as well as  $\mathcal{H} = QHQ$  and  $\mathcal{H} = \hat{Q}H\hat{Q}$ . The last case is the one we are primarily interested in. The solutions of the above equation are assumed to be quadratically integrable (which is a somewhat stronger condition than assuming  $\lim_{r \rightarrow \infty} \gamma = 0$ ). This is sufficient to guarantee that solutions belonging to two different energies are orthonormal

$$\langle \gamma(\varepsilon), \gamma(\varepsilon') \rangle = \delta_{\varepsilon\varepsilon'} \quad (\text{A1.2})$$

Because the functions are quadratically integrable, the rhs of (A1.2) is strictly a Kronecker delta. This means that no matter how close  $\varepsilon$  is to  $\varepsilon'$  the inner product is zero unless  $\varepsilon$  is precisely equal to  $\varepsilon'$ .

Now, contrary to what we want to demonstrate, let us assume that solutions exist for a continuous range of  $\varepsilon$ , so that  $\gamma$  is a continuous function of  $\varepsilon$ . Let us further assume that  $\gamma$  can be expanded in a Taylor series

$$\gamma(\varepsilon') = \gamma(\varepsilon) + (\Delta\varepsilon) \left[ \frac{\partial \gamma(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon=\varepsilon'} + O(\Delta\varepsilon^2), \quad (\text{A1.3})$$

where  $\Delta\varepsilon = \varepsilon' - \varepsilon$ . Substituting (A1.3) into (A1.2) yields

$$1 + O(\Delta\varepsilon) = 0, \quad (\text{A1.4})$$

Finally taking the limit  $\Delta\mathcal{E} \rightarrow 0$ , we have the desired contradiction  $1 = 0$ .

This implies then that the values of  $\mathcal{E}$  cannot form a continuum. (It does not say that the discrete values  $\mathcal{E}_n$  cannot cluster arbitrarily close to each other as in fact they do in the hydrogenic bound state problem.) This demonstration only applies for a  $\hat{Q}$  operator constructed from exact target eigenfunctions.

## Appendix II

Equivalence of  $\hat{Q}_a$  and  $\hat{Q}_b$  for Closed Shell Targets

It can be seen from (2.4) and (2.3) that the difference between  $\hat{Q}_a$  and  $\hat{Q}_b$  involves products of two, or more than two, distinct  $P_i$ . We shall show that

$$P_i P_j \psi = 0 \quad (i \neq j) \quad (\text{A2.1})$$

when the target state from which the  $P_i$  are constructed is a closed shell Slater determinant. Specifically the target state is

$$\bar{\Phi}^N(j^{-1}) = \begin{vmatrix} \psi_1(r_1)\alpha(1) & \psi_1(r_1)\beta(1) & \dots & \psi_{\frac{N}{2}}(r_1)\beta(1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_{j-1})\alpha(j-1) & \dots & \dots & \psi_{\frac{N}{2}}(r_{j-1})\beta(j-1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_{j+1})\alpha(j+1) & \dots & \dots & \psi_{\frac{N}{2}}(r_{j+1})\beta(j+1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_{N+1})\alpha(N+1) & \dots & \dots & \psi_{\frac{N}{2}}(r_{N+1})\beta(N+1) \end{vmatrix} \quad (\text{A2.2})$$

The total wave function  $\Psi$  is arbitrary but completely antisymmetric, therefore insofar as its projection on  $\Phi^N(j^{-1})$  goes, it is completely equivalent to write  $\Psi$  in the form

$$\Psi \rightarrow \begin{vmatrix} F(r_j)\chi_j(j) & \dots & \dots & F(r_j)\chi_j(j) \\ \vdots & & & \vdots \\ F(r_j)\chi_j(j) & \dots & \dots & F(r_j)\chi_j(j) \end{vmatrix}$$

$\vdots$        $\vdots$   
 $\Phi^N(j^{-1})$

From (A2.3) however it is clear since  $\chi_\gamma(j)$  is either  $\alpha(j)$  or  $\beta(j)$  and since all radial orbitals in  $\Phi^N$  are occupied, that we can choose:

$$\int F(r) \varphi_n(r) dr = 0, \quad n = 1, 2, \dots, \frac{N}{2}. \quad (\text{A2.4})$$

(The nonorthogonal parts of  $F$  can only be such as to make various rows of the determinant on the rhs (A2.3) identical to each other, thus they make no contribution.)

Now by straightforward evaluation

$$P_j \Psi = \Phi^{(N)}(j^{-1}) F(r_j) \chi_\gamma(j), \quad (\text{A2.5})$$

so that

$$P_i P_j = \Phi^{(N)}(i^{-1}) \langle \Phi^{(N)}(i^{-1}) \Phi^{(N)}(j^{-1}) F(r_j) \chi_\gamma(j) \rangle. \quad (\text{A2.6})$$

Expand the  $\Phi$ 's by minors:

$$\Phi^{(N)}(i^{-1}) = \sum_{\substack{m \\ \mu=1,2}} \varphi_m(r_i) \chi_\mu(i) \Phi_{m,\mu}^{(N-1)}(j^{-1}, i^{-1}) (-1)^{p_{m\mu}} \quad (\text{A2.7a})$$

$$\Phi^{(N)}(j^{-1}) = \sum_{\substack{n \\ \nu=1,2}} \varphi_n(r_j) \chi_\nu(j) \Phi_{n,\nu}^{(N-1)}(j^{-1}, i^{-1}) (-1)^{p_{n\nu}}. \quad (\text{A2.7b})$$

Use the orthonormality

$$\langle \Phi_{n,\nu}^{(N-1)}(j^{-1}, i^{-1}) \Phi_{m,\mu}^{(N-1)}(j^{-1}, i^{-1}) \rangle = \delta_{nm} \delta_{\nu\mu} \quad (\text{A2.8})$$

(which implies  $(-1)^{p_{m\mu} + p_{n\nu}} \delta_{mn} \delta_{\mu\nu} = \delta_{mn} \delta_{\mu\nu}$  in (A2.6) to obtain

$$\begin{aligned} P_i P_j \psi &= \sum_{n,v} \psi_n(x) \chi_v(y) \langle \psi_n(y) \chi_v(y) F(y) \chi_v(y) \rangle \\ &= \left[ \sum_n \psi_n(x) \langle \psi_n(y) F(y) \rangle \right] \chi_v(y) . \end{aligned} \quad (\text{A2.9})$$

And now using (A2.4), we have our desired result

$$P_i P_j \psi = 0. \quad (\text{A2.10})$$

This proves (A2.1); since

$$\hat{Q}_a - \hat{Q}_b = \sum_{\sigma=2}^{N'+1} (-1)^\sigma \prod_{i,j,\dots (\text{distinct})}^{\sigma} (P_i P_j \dots) \quad (\text{A2.11a})$$

and the number of distinct projectors  $P_i$  in each product starts with  $(\sigma = 2)$ , it follows from (A2.10) that any larger number of distinct projectors acting on  $\psi$  is zero. Hence

$$(\hat{Q}_a - \hat{Q}_b) \psi = 0. \quad (\text{A2.11b})$$

From (A2.10) one can also trivially show

$$\hat{Q}_{a,b}^2 \psi = \hat{Q}_{a,b} \psi, \quad (\text{A2.12a})$$

and

$$\hat{P}_{a,b}^2 \psi = \hat{P}_{a,b} \psi. \quad (\text{A2.12b})$$

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Table I.  $^1S$  Eigenvalues (in eV) of  $\hat{Q}H\hat{Q}$  for One Electron Targets<sup>a</sup>

System	e - He <sup>+</sup>		e - H
$n$	$\epsilon_2 - E_0$	$\epsilon_3 - E_0$	$\epsilon_2 - E_0$
13	33.2415	37.506	9.5607
22	33.2290	37.4825	9.5431
34	33.2281	37.4785	9.5410
50	33.2278	37.478	9.5406
Precision <sup>b</sup> QHQ	33.2267	37.471	9.5387

a.  $E_0$  is the ground state energy of the target system

b. Based on a 50 term Hylleraas calculation of Bhatia, Temkin,  
and Perkins, Ref. 9.

Table II:  $^2S$  Autoionization State of  $\text{He}^-$  Using  
Angle-Independent Wave Function (5.1)<sup>a</sup>

$n$		$\hat{\epsilon}_1 - E_0$	$\hat{\epsilon}_1 - E_0$	$\Gamma$	$\Gamma$
	$\tilde{\phi}_0 \rightarrow$	closed	open	closed	open
10		20.55	20.66	0.0087	
22		20.14	20.14	0.0029	
34		20.06	20.05	0.0044	
50		20.02	20.01	0.0039	
70		19.99	19.98	0.0044	

a. Results in eV; nonlinear parameters optimized only for the  $n = 70$  term results.

Table III:  $^2S$  Autoionization State of  $\text{He}^-$  Using  
Twelve Configuration Interaction Wave Function (5.3)<sup>a</sup>

$\alpha_{3s}$	$\hat{\mathcal{E}}_1 - E_0$	$\alpha_{4s}$	$\hat{\mathcal{E}}_1 - E_0$	$\alpha_{4p}$	$\mathcal{E}_1 - E_0$
.3378	19.4232	.9743	19.4206	.4973	19.42033
.3412	19.4227	.9837	19.4205	.5023	19.42028
.3446	19.4223	.9930	19.4204		
.3480	19.4219	1.0024	19.4203		
.3514	19.4217				
.3548	19.4215				
.3582	19.4214				
.3617	19.4214				

a. Results (in eV) based on a twelve configuration expansion  $1s(2s)^2$

$1s(2s3s)$   $1s(2p)^2$   $(1s\ 2p)\ 3p$   $(1s2s)4s$   $1s(2s4s)$   $(1s2s)3s$   
 $1s(3s)^2$   $(1s2p)\ 4p$   $1s(2p4p)$   $1s(3p)^2$   $1s\ (2p3p)$ .

This table gives results with respect to the variations of the nonlinear parameters specified. The remaining nonlinear parameters were approximately optimized from previous calculations and had the value  $\alpha_{1s} = 1.995$ ,  $\alpha_{2s} = .5508$ ,  $\alpha_{2p} = .6008$ ,

$\alpha_{2p} = .4455$ .